# POLYCARBONATE WITH FUNCTIONALIZED GRAPHITE NANOFIBERS (GNF) AND THE STUDY OF ITS THERMAL AND MECHANICAL PROPERTIES

by

MOHD NIZAR BIN MOHD NASIR
13164

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

UNIVERSITI TEKNOLOGI PETRONAS

# CERTIFICATION OF APPROVAL

**Polycarbonate with Functionalized Graphite Nanofibers (GNF)**
**and**
**The Study of Its Thermal and Mechanical Properties**

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Mohd Nizar Bin Mohd Nasir
(13164)

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Approval by:

(Dr Maziyar Sabet)

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UNIVERSITI TEKNOLOGI PETRONAS

# CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHD NIZAR BIN MOHD NASIR

# ABSTRACT

The present study described the process of producing polycarbonate with functionalized graphite nanofiber (GNF) composite and its properties. To improve the solubility of GNF, it will have to go through functionalization which is also known as oxidation. Before functionalization, the GNF have to undergo acid wash process to eliminate metal catalyst in the raw GNF at the same time removing impurities and increase the purity. Acid wash was done by using 2 Molar (M) of hydrochloric acid and 1 hour of stirring using a mechanical stirrer. After metal elimination process, the GNF was functionalized for 4 hours in 4M nitric acid by using double sonication system; which was using both ultrasonic bath and ultrasonic probe at the same time, to increase efficiency. The acid treatment chemically modified the hydrophobic and inert nature of the surface of raw GNF by attaching functional group such as carboxyl group (COOH) which were detected by using Fourier Transform Infrared Microscopy (FTIR) analysis. The morphology and surface of the GNF were studied from Field Emission Scanning Electron Microscopy (FESEM). Then, the enhance polymer plastic were prepared by solution blending method. Dispersion of GNF within the polymer was observed by microscopic imaging. The study then investigated into the mechanical and thermal properties of the polycarbonate-GNF by Thermo Gravimetric Analysis (TGA) and Universal Testing Machine. For this research, 0.5wt% gives the better dispersion without aggregation and a significant increase in the properties compared to the samples of 1wt% and 2wt% where the fibers agglomerate; decreasing the nano-composites potential.

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# ABBREVIATION

| | |
|---|---|
| AW | Acid Washed |
| CNF | Carbon Nanofibers |
| CNT | Carbon Nanotubes |
| FESEM | Field Emission Scanning Electron Microscopy |
| FTIR | Fourier Transform Infrared |
| GNF | Graphite Nanofibers |
| GO | Graphite Oxide |
| MWCNT | Multi-Walled Carbon Nanotubes |
| PC | Polycarbonate |
| PC-GNF | Polycarbonate with Graphite Nanofibers |
| SEM | Scanning Electron Microscopy |
| SWCNT | Single-Walled Carbon Nanotubes |
| TGA | Thermo Gravimetric Analysis |

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# CHAPTER 1
# INTPRODUCTION

## 1.1 BACKGROUND

Polycarbonates (PC) were first prepared by Einhorn in 1898 and extensively researched until 1930 where they were discarded. Research was then started in the mid 1950's by General Electric (UL IDES). It was in 1953, polycarbonate was discovered by Dr. H. Schnell at Bayer AG, Germany, and by D. W. Fox at General Electric Company, USA working independently. In the late 1950's polycarbonate popularity expanded to a global community and began to be used in commercial applications (Plactics Europe).

Xanthos (2005) stated that polymer composites are mixtures of polymers with inorganic or organic additives that have certain geometries. Thus, they are made of two or more components and two or more phases. The additives may be continuous and embedded in the polymer in orderly arrangements that extent throughout the dimension of the product. Conventionally, additives or filler's main contribution was in lowering the cost of materials by replacing the more expensive polymer; where their unfavorable features fairly increase the polymers' modulus and either unaffected the polymers' strength or even decrease it. However, the term reinforcing filler or additive have been reinvented where the properties of the additive; shape, form, and/or surface chemistry of which have been suitably modified with the aim of improving the mechanical properties of the polymer. Mascia (1974) proposed that fillers have their specific function, such as their ability to modify mechanical, electrical or thermal properties, flame retardancy, processing characteristics, solvent permeability, or merely formulation costs. Earlier nanocomposites used nanoscale fillers such as carbon black, carbon fibers and nanotubes, and graphite are said to be able to modify polymers' surface, mechanical,

electrical and magnetic, and thermal properties (Moniruzzaman, M. & Winey, K., 2006; Xanthos, 2005).

GNF is a product similar to carbon black produces by other manufacturer in industry. The different is graphite nanofibers is in nano-scale structure and comes with the superior quality that does not exist in carbon black. The component of carbon black is mainly made up by carbon. Besides, they are also the same like carbon nanotubes (CNT) with different physical structure. A large amount of carbon black is mainly contributed in tires as excellent rubber reinforcement. Furthermore, carbon black and CNT are used in various other applications as an electric conductive agent, thermal conductive agent, additive to improve rheology and increasing strength in metal while reducing its' weight.

The main application of the functionalized GNF or CNT is for dispersion as the process improves its solubility in solvents such as water and polymers. It have been use with Liquid Crystal Polymer (LCP) for electromagnetic interference shielding (Yang, S. et al.,2005), mix with polypropylene to improve its electrical thermal and mechanical properties (Seo, M. et al., 2005),, and mix with syndiotactic polystyrene to increase melting point and electrical resistivity (Kumar, S. et al., 2007). This shows that, by chemically modifying the GNF, it will expand its usage for a wider variety of applications and industry.

## 1.2 PROBLEM STATEMENT

Polycarbonate; a thermoplastic polymer with good properties but are subjected to stress cracking, besides other weaknesses. Additives are used to improve the mechanical, thermal and electrical properties of polycarbonate where it previous researches, carbon nanotube, carbon black and graphene have been used to do so but not yet using graphite

nanofibers (GNF). The carbon based fibers is known to be hydrophobic, therefore a proper blending method should be develop to achieve the nanocomposite product.

## 1.3 OBJECTIVES

The main purposes of this paper are:-

- To study the blending of GNF and Polycarbonate.
- To study the ultimate product composites mechanical, and thermal properties.
- To study the effect of GNF concentration in the polymer composite's properties.

## 1.4 SCOPE OF STUDY

In order to achieve the Polycarbonate GNF mixture, series of experiments are needed to be done to eliminate the metal catalyst in the raw GNF, functionalization of GNF and the blending process. Field Emission Scanning Electron Microscopy (FESEM) will be used to study the morphology and size of the GNF and Optical Microscopy to study the dispersion of GNF in the plastic film. Fourier Transform Infrared Spectroscopy (FTIR) test will be conducted to study the functionalization of GNF and the functional group attached to it. As for the property test, Thermogavimetric Analysis (TGA) will be used for temperature property testing, tensile modulus and stress-strain test for mechanical properties testing.

## 1.5 RELEVENCY OF PROJECT

The project is important to study the application of a quite new product in the market which is Graphite Nanofibers (GNF) besides improving the properties of plastic polymer, Polycarbonate (PC). This project PC-GNF is compatible with the author's field of study which is chemical engineering. In order to came up with the procedure to conduct the experiment for all three stages from eliminating metal, functionalizing GNF and mixing PC-GNF required basic engineering and chemical knowledge, common sense in safety and environment practices and most importantly is to have high quality work ethics. All in all, to complete this project, it needed the knowledge learnt in classroom and more. It educate to applied all that have been thought by the lecturer and use the tools given by the university and supervisor to self-learn and stand on owns feet to solve a problem or to came up with a solution.

## 1.6 FEASIBILITY OF PROJECT WITHIN THE SCOPE AND TIME FRAME

The Polycarbonate GNF project is estimated to be completed in 26 weeks throughout the duration of the Final Year Project 1 (FYP1) and Final Year Project 2 (FYP2). The time allocated for FYP1 are 14 weeks where it will be focusing more on finding literatures and research on the polycarbonate and GNF as well as the methodology of the experiments to achieve it while FYP2 will be more on developing the product composite, property testing, and studying its' results against past researched. Based from the Gantt chart (Appendix 1) it shows that this project can be done within the time frame if not earlier.

# CHAPTER 2
# LITERATURE REVIEW

## 2.1 CRITICAL ANALYSIS LITERATURE

### 2.1.1 MATERIAL

Sumry (2010) mentioned that polycarbonate is in a group of thermoplastic polymer and can be very easy worked and molded into different shapes and can also be thermoformed which make polycarbonate very much in used in the modern chemistry industry because there are a number of advantages and disadvantages to polycarbonate. They show great capacities for temperature resistance, impact resistance as well as for optical properties. Due to the properties, manufacturers are designing items not only for the household but for use in laboratories and in industry. Besides the fact it can be injected into various objects which allowed it to be used for discs, bottles, glasses, break resistant lenses, and audio player cases. Although with the remarkable properties polycarbonate have, (UL IDES) stated that it also subjected to stress cracking, aromatic sensitive, fair chemical resistance, and degrades upon extended residence time in processing equipment.

Graphite Nanofibers or simply known as GNF is produced with the catalytic thermal decomposition method or the partial combustion method using hydrocarbons such as natural gas as raw material (Mitsubishi Chemicals,2006). One of the methods to produce GNF is by thermal decomposition with the presence of catalyst. As the name implies, the reaction is a moderately endothermic process which means it requires energy or heat to make up the reaction (Wang & Baker, 2005). It can be seen from the reaction stoichiometry, $CH_4 \rightarrow C+2H_2$, one mol of natural gas (mainly methane), will produce one mol of carbon and two moles of hydrogen. The product produces are light in weight, stronger than steel and has excellent properties for thermal and electrical conductivity.

Graphite nanofibers feature single crystal graphite characteristics imparting high surface area for rapid kinetics and high degree of crystallinity for higher conductivity. The product have hexagonal shape multiwalled nanotubes with aligned end edges feature provides easy dispersion in non-aqueous media such as plastics and enables high performance with low doping (Platinum Energy, 2012). Due to carbon fibers high specific tensile modulus, strength and excellent electrical and thermal properties, carbon fibers are widely used nowadays as reinforcements for polymer matrices in many high-technology applications (Sandler et al., 2002).

### 2.1.2 METAL ELIMINATION / PURIFICATION

On account of the catalyst used to produce the nanofibers are metal based, it needed to be eliminated first before other process to increase the purity of the product or avoid further side reactions and unwanted results. (Naseh et al., 2009) asserted that they use hydrochloric acid to remove the metal catalyst, by refluxing method for 2 hours and the remaining metal will be removed during functionalization process as it also uses acid treatment. When a reaction between an acid and a metal oxide occurred, it will form a salt and water as the only product (Green and Perry, 2007). While if metal react with acid, it will produce salt and hydrogen gas. This process is crucial to the properties of the end result or polymer nanocomposite as researched done by (Li, Z. et al., 2011) discovered that metal catalyst residues in carbon nanotubes (CNTs) will decrease the thermal stability of polymer/CNT where it explains the results obtained by different researchers that are found contradicting especially on a large loading of CNT. The metal impurity present in the CNTs is one of the key differences.

### 2.1.3 FUNCTIONALIZATION / OXIDATION

Dispersing nanotubes into solvents has proven to be very difficult as the strongly held ropes are not easily broken up into individual tubes by either temperature or by solvent (Rai et al., 2007) affected by attractive Van der Waals interaction among themselves. Naseh et al., (2009) and Tour et al., (2007) stated that, to improve the interaction with foreign molecules such as the solubility or suspension ability and processebility of the nanotubes in common organic solvents and/or water, it is necessary to modify the hydrophobic and inert nature of the surface of as-prepared nanotubes. Chemical modification also known as oxidation or functionalization of carbon nanotubes does not change the electronic and bulk properties of these materials (Tour et al., 2007).

Oxidation creates carboxylic acid groups (COOH) on the nanotubes' surface to provide opportunity to synthesize many different functional groups on it as well as polymer grafted to it (Tchoul et al., 2007). Tchoul and colleagues also mentioned that the oxidation conditions should be chosen carefully, as the process may result in structural defect, shortening of tubes, accumulation of carbonaceous impurities, and overall loss of material. The chemical modification uses acid treatment to attached carboxylic groups to the nanofibers surfaces (Kumar et al., 2007) and form the literature screening, shows that nitric acid, HNO3 is commonly used to oxidized the nanotubes next to nitric acid and sulphuric acid mixture with ratio of 1:3 as specified by (Tchoul et al., 2007; Kumar et al., 2007; Aziah et al., 2012).

Tour et al., (2007) mentioned that suitable acid media include any acidic medium capable of dispersing nanotubes in a substantially individualized tubes where in some embodiments, the acid medium is or comprises of an oxoacid; H2SO4, H3PO4, HClO4

and HNO3. Most researchers use concentrated acid for the treatment, as said by (Rosca et al., 2005), acid concentration amplified by temperature has a great influence on nanotubes solubility. In a study using lower concentration of acid, (Aziah et al., 2007) uses water bath ultrasonic Branson 2000 with 6M of HNO3/H2SO4 and temperature of 40 degree Celsius for 4 hours. Sonication of nanotubes during functionalization process will break up nanotubes bundles and expose the sidewalls to functionalized agent (Tour et al., 2007). The longer the sonication treatment, it will increase the improvement in the disability (Tchoul et al., 2007).

Caneba et al., (2010) stated that for more significantly increase in dispersion efficiency of carbon nanotubes with shorter time consume, higher voltage and less overall power consumption. Based on superposition principle, thermal measurements of dispersing fluid show temperature increases proportionate with the power level of two ultrasonic sources the use of double ultrasonic source will give the better result

### 2.1.4 MIXING FILLERS/ADDITIVE AND POLYMER

Hsiao (2012) had researched on the polymer wrapping of carbon nanotubes and have come up with 3 methods which are by in-situ polymerization method, solution process and melt-mixing. For the in-situ method, the monomers and nanotubes are mixed well in a solution and then it is polymerized. Solution process will obtain the carbon nanotubes/polymer composites by re-precipitation or removing the solvent from the mixture while as for melt mixing, the nanotubes and polymer are mixed at high temperature that are normally above the glass transition temperature of the polymer by mechanical mixing. (Fu et al., 2007) imparted that in order to incorporate the carbon nanotube component in the viscoelastic fluid, sonication is needed.

Moniruzzaman, M. & Winey, K. (2006) stated that solution blending is the most common technique for producing polymer nano-composites because it is amenable to small sample sizes and effective. Major steps in solution blending are dispersion of nanotubes, mix with polymer and recover the composite by casting a film or precipitation. High-power sonication can be used to achieve a stable suspension of nanotubes or nanotubes/polymer mixture in solvent. Besides, surfactant is used to disperse higher loadings of nanotubes but as shown by (Sundararajan et al., 2004) the surfactant Triton X-100 induced crystallization in polycarbonate, in addition to able to alter the polymer matrix. They mentioned that the mesomorphic order prompted by the surfactant in various atactic polymers was due to the hydrogen bonding of the side group of the polymer with the polar group of the surfactant and the interdigitation of the alkyl part.

This leads to another alternative aside using surfactant, which is by using functionalized nanotubes or carbon fibers as they will have functional group attached to them; carboxyl group (COOH) and hydroxyl group (OH) that will induced hydrogen bonding between the nano-composites. Moniruzzaman, M. & Winey, K. (2006) also wrote that functionalization of nanotubes can improve its' dispersion and interfacial adhesion to the polymer matrix. Yoonessi & Gaier (2010) says that dispersion, concentration, aggregation and orientation of the nanoparticles have a significant impact on the nano-composites' electrical conductivity and percolation threshold. While the size of the suspended nanoparticles provide the interfacial area for stress transfer to the polymer matrices where the smaller the particle size, it will increase the interfacial area (Moniruzzaman, M. & Winey, K., 2006).

### 2.1.5 PROPERTY TESTINGS/ EXPECTED RESULTS

Kim, K. & Jo, W., (2009) founds that the mechanical properties of multi-walled carbon nanotube (MWCNT) and polycarbonate composite are notably decrease as compared to neat polycarbonate. The results were reasoned as the weak interfacial adhesion between MWCNTs and the poor dispersion of it within the polycarbonate due to it was not functionalized. As functionalizing agent was added, it was found that the tensile strength, young modulus and elongation-at-break increases till optimum of 0.5wt% before decreases with added more weight percent caused by MWCNTs aggregation in polycarbonate. Liu, S. et al., (2010) divided the mechanical studies into surface and bulk mechanical properties. The surface studies covered wear resistance identified by Scanning Electron Microscopy (SEM) images of surface morphology and shore hardness test. The shore hardness (Hs) increased evidently up to 5wt% of MWCNTs in polymer composites and it was found that higher loading of 5wt% MWCNTs to be aggregated in polymer matrix, in which causing apparent decrease in bulk mechanical properties. The bulk studies of tensile and flexural strength that gave the best performance are the polymer composites with 3wt% before it decreases.

The electrical conductivities of the polycarbonate/MWCNTs composite increases with the increase dispersion of MWCNTs in polymer matrix and at a best dispersion 0.5wt% could give substantial results (Kim, K. & Jo, W., 2009). Kumar, S. et al. (2010), discovered that DC conductivity only increase slightly when conducting network is not formed at low loadings of 0.5 and 1wt% which is from $10^{-14}$ S/m to $10^{-12}$ S/m. The conductivity increased significantly from 1 to 3wt% up to 10 orders of magnitude, from $10^{-12}$ S/m to $10^{-2}$ S/m, showing evolution of insulator to conducting phase. The addition of more nanofiber fillers beyond 3wt% will only improve the conductivity marginally.

Higginbotham A. et al. (2009), stated that Graphite Oxide (GO) with polycarbonate composites gives the best results compared to GO with high-impact polystyrene mixture or with acrylonitrile butadiene styrene mixture. The self-extinguishing times for % and 10wt% of GO in polycarbonate were immediate after removal of the flame. The temperature of degradation onset was 471°C, 475°C and 477°C for the 1%, 5% and 10% of GO in polycarbonate which concluded GO does not notably altered the thermal stability of the polymer. Kumar S. et al. (2010), learnt that addition of CNF increases the onset and end degradation temperature of polycarbonate nano-composites. The degradation temperature increases from 390°C of pure PC to 408°C and 444°C at 3 and 5wt% loading of CNF within the polymer nano-composites.

## 2.2 RELEVENCY AND RECENTNESS OF LITERATURE

The literature is important to gives critical view and understanding about functionalizing graphite nanofibers (GNF) including its backgrounds, method of preparations, properties, and expected results. The more important the source of these literature are taken from utmost 10 years back but most are published about 2 to 7 years which are quite recent. Since GNF are a new product in the market, there are not many researched done on it compared to other carbon products such as carbon black or carbon nanotubes. Due to that, the author mostly refer to the process involving carbon nanotubes as they are close to GNF in term of chemical properties, with different physical structures.

While the literature on the polycarbonate and its blending processes were also based with other carbon based additive. These literatures found were utmost a decade back which is found to be still update with supportive recent literatures to back it up.

# CHAPTER 3
# METHODOLOGY

## 3.1 PROCESS METHODOLOGY

### 3.1.1 ACID PREPARATION

1. Weigh acid stock solution by using beaker.
2. Pour some amount of distilled water in the volumetric flask first.
3. Pour the weighed amount of the acid stock in the volumetric flask that is filled with distilled water.
4. Fill up the volumetric flask with distilled water until its level reaches the marking point.

Weight of acid stock that must be prepared:-

HCl – 37% v/v. Specific gravity: 1.19 g/ml and molecular weight of 36.5 g/mol.

37ml/100ml or 370ml/1L x 1.19 g/ml = 440.3 g/L

Molarity, M = 440.3/36.5 = 12.06M ~ 12M

Compounding 500ml of 2M HCl:

$$M_1V_1 = M_2V_2$$

$$(2)(500) = (12)(x)$$

$$x = \frac{(2)(500)}{12} = 83.33\text{ml}$$

**Table 3.1.1: Acid Stock to Acid Sample Solution**

| Acid stock | Stock form | Stock concentration | Solution concentration | Weight / Volume |
|---|---|---|---|---|
| **Hydrochloric acid, HCl** | liquid | 37% | 2 molar | 83.3 ml |
| **Nitric acid, HNO3** | liquid | 69-70% | 4 molar | 133.33 ml |

### 3.1.2 METAL ELIMINATION

By using acid wash method.

1. Take 70 gram of raw graphite nanofiber, GNF and grind the sample.
2. Measure the 2 molar, M of Hydrochloric acid; make sure the volume of the acid was in excess than the volume needed to convert the metal into metal chloride.

$$Ni + 2HCl \rightarrow NiCl_2 + H_2$$

Volume of minimum 2M HCl required :

$$\text{V HCl} = 70g\ GNF \times \frac{a\ g\ Ni}{b\ g\ GNF} \times \frac{1\ mol\ Ni}{58.69\ g\ Ni} \times \frac{2\ mol\ HCl}{1\ mol\ Ni} \times \frac{L\ HCl}{2\ mol\ HCl}$$

Where,

Molecular mass of Nickel = 58.69 g/mol

Yield of GNF = $\frac{b}{a}$ g GNF/g catalyst

3. Stir the mixture for 1 hour.
4. After 1 hour stirring, wait for the sample to sediment at the bottom of the beaker.
5. Dispose the used acid in a container. The acid can be reused for another washing.
6. Mix the collected sediment with distilled water. Make sure the weight of distilled water was five times the weight of collected sediment. Stir the mixture for a few minutes and wait the sample to sediment at the bottom of the beaker.
7. Dispose the distilled water in the disposal tank.
8. Repeat step 4 and 5 until pH of the mixture reaches 6.
9. Dry the sample in oven for 12 hours. Set the temperature to 90°C.
10. Collect the dried sample.
11. Repeat the experiment for a few times by changing the period of stirring and molarity of acid used.

### 3.1.3 FUNCTIONALIZATION OF GNF (Double Sonication method)

1. Take 50 gram of GNF that already undergo metal elimination acid wash.
2. Measure the 4M of Nitric acid; make sure the weight of the acid was five times of the weight of the sample. Mix the sample with acid solution in a beaker.
3. Equipment and parameter used;
   i) Ultrasonic probe
      - Model : Labsonic M
      - Voltage : 230 V
      - Frequency : 50 kHz
      - Cycle : 1
      - Amplitude : 100%
   ii) Ultrasonic water bath
      - Model : Bath ULTRASonik 57X
      - Power : 50%
      - Voltage : 230V
      - Frequency : 50/60 kHz

4. Set up the apparatus ;

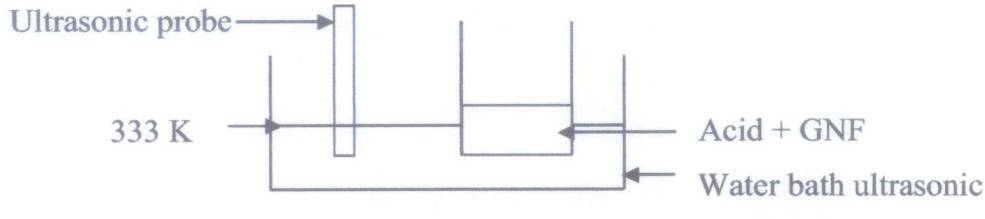



**Figure 3.1: Double Sonication Experimental Diagram**

5. Place the ultrasonic probe and beaker containing the GNF acid mixture opposite to each other in the ultrasonic water bath. Switched on the equipment.
6. Stir for 10 minutes every half an hour.

7. After 4 hours, take the sample beaker out of the water bath and wait for the sample to sediment at the bottom of the beaker. At the mean time shut down all the equipment.
8. Dispose the used acid in a container.
9. Mix the collected sediment with distilled water. Make sure the weight of distilled water was five times the weight of collected sediment. Stir the mixture for a few minutes and wait the sample to sediment at the bottom of the beaker.
10. Dispose the distilled water in the disposal tank.
11. Repeat step 8 and 9 until pH of the mixture reaches 6.
12. Dry the sample in oven for 12 hours. Set the temperature to 90°C.
13. Collect the dried sample.
14. Product sample was then sent for FTIR analysis to study if the functional group that were supposed to attach to the GNF as a result of the experiment.

### 3.1.4 BLENDING OF POLYCARBONATE AND GNF

Method: Solution Blending

1. Dried the Polycarbonate for 24 hours.
2. Weight Polycarbonate.
3. Dissolve the polycarbonate with methylene-chloride, CH2Cl2 as solvent at room temperature and sonication for 1 hour.
4. Disperse 0.02 wt% GNF in the 20ml of CH2Cl2 by 1 hour sonication.
5. Mix the polycarbonate-CH2Cl2 solution into the GNF-CH2Cl2 solution slowly within 5 minutes.
6. The mixture was then placed in an ultrasonic bath for 45 minutes.
7. Quickly the solution was then poured into a waxed petri dish.
8. Then, the sample was dried in a vacuum oven at 30 degree Celsius for the next 24 hours.
9. Repeat the process using different concentration of GNF; 0.04wt%, 0.05wt%, and 0.10wt%. The samples are carefully not to be exposed to moisture.

10. Analysed all the samples for its' mechanical, and thermal properties. By using TGA, optical microscopy, and mechanical properties universal testing instrument.

**Table 3.1.2: PC-GNF Matrix**

| Concentration GNF (wt%) | Per sample | | | Per batch (16 samples) | | |
|---|---|---|---|---|---|---|
| | GNF | PC | CH2Cl2 | GNF | PC | CH2Cl2 |
| 0.05 | 0.00075g | 1.5g | 10ml | 0.012g | 24g | 160ml |
| 0.08 | 0.0012g | 1.5g | 10ml | 0.0192g | 24g | 160ml |
| 0.1 | 0.0015g | 1.5g | 10ml | 0.024g | 24g | 160ml |
| 0.5 | 0.0075g | 1.5g | 10ml | 0.12g | 24g | 160ml |
| 1.0 | 0.015g | 1.5g | 10ml | 0.24g | 24g | 160ml |
| 2.0 | 0.030g | 1.5g | 10ml | 0.48g | 24g | 160ml |
| 3.0 | 0.045g | 1.5g | 10ml | 0.72g | 24g | 160ml |

***Note:*** *Pictures of the experiments are in appendix*

## 3.2 PROJECT ACTIVITIES

There are four parts of the project; research, experiments, analysis, and compiling and reporting. Research was done on the earlier section of completing the project and throughout while experiments will be done on the 2nd half of the time frame where it will be then divided into 4 stages; metal elimination in raw GNF, functionalization of GNF, blending Polycarbonate and GNF and finally properties testing of the final product. Later those results will be studied and analyzed and compares with previous similar or almost similar project. Lastly, the all the findings and outcome of the project were compiled and put in a thesis report for documentation and grading. Also, it was to be presented to esteem examiners.

## 3.3 KEYMILESTONES

**FYP1**

- Week 6 : Submission of Extended Proposal
- Week 8 : Proposal Defence
- Week 13 : Submission of Interim Draft Report
- Week 14 : Submission of Interim Report

**FYP2**

- Week 8 : Submission of Progress Report
- Week 11 : Pre-SEDEX
- Week 12 : Submission of Dissertation (soft bound)
- Week 12 : Submission of Technical Paper
- Week 13 : Oral Presentation
- Week 14 : Submission of Project Dissertation (hard bound)

## 3.4 TOOLS AND EQUIPMENT

These are the materials, apparatus and equipment being used in Polycarbonate GNF project.

**Table 3.4: Tools being used in Polycarbonate GNF Blending project**

| | Acid Preparation | Metal Elimination | Functionalization | Blending PC GNF |
|---|---|---|---|---|
| **Materials** | | | | |
| GNF | | / | | |
| GNF acid washed(AW) | | | / | |
| GNF AW + Oxidized | | | | / |
| Hydrochloric Acid, HCL | / | / | | |
| Nitric Acid, HNO3 | / | | / | |
| Polycarbonate polymer | | | | / |
| Methylene Chloride, CH2Cl2 | | | | / |
| **Apparatus** | | | | |
| Beaker | | / | / | / |
| Measuring cylinder | / | / | / | / |
| Glass rod | | / | / | / |
| Glass funnel | | / | / | |
| volumetric flask | / | | | |
| Aluminium mold | | | | / |
| **Equipment** | | | | |
| Mechanical Stirrer | | / | | |
| Weight balance | | / | / | / |
| Drying oven | | / | / | / |
| Ultrasonic probe | | | / | |
| Ultrasonic water bath | | | / | / |

# CHAPTER 4
# RESULTS AND DISCUSSION

## 4.1 DISPERSION TEST

Dispersion test have been done on the functionalized GNF with methylene chloride as solvent to check whether it could be dispersed in the solvent for more than 1 hour to prove it have been oxidized.

**Figure 4.1.1 : Dispersion Test at time 0min**

**Figure 4.1.2 : Dispersion Test after 24hours**

Figure 4.1.1 shows the test at time 0min, after 1 hour of sonication and Figure 4.1.2 is the image of the test after 24 hours. From the images, it can be seen that there are particles of GNF still dispersed in the solvent and some suspended due to being larger particles and the solvent being over saturated.

## 4.2 FOURIER TRANSFORM INFRARED MICROSCOPY ANALYSIS (FTIR)

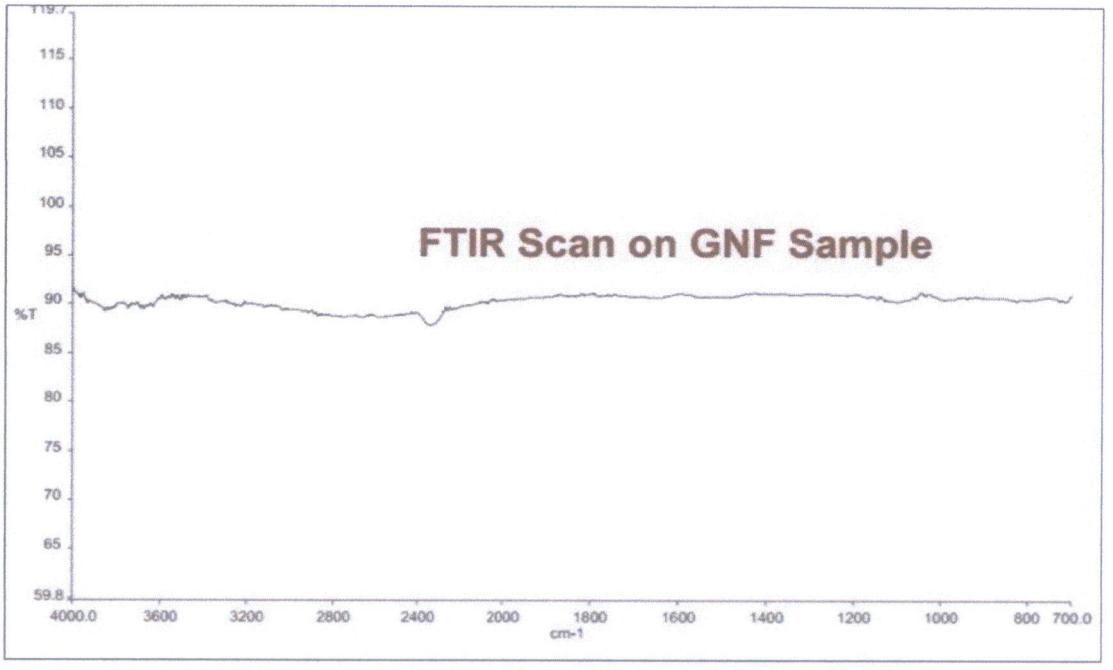



**Figure 4.2.1 : FTIR Analysis of Raw Graphite Nanofibers**

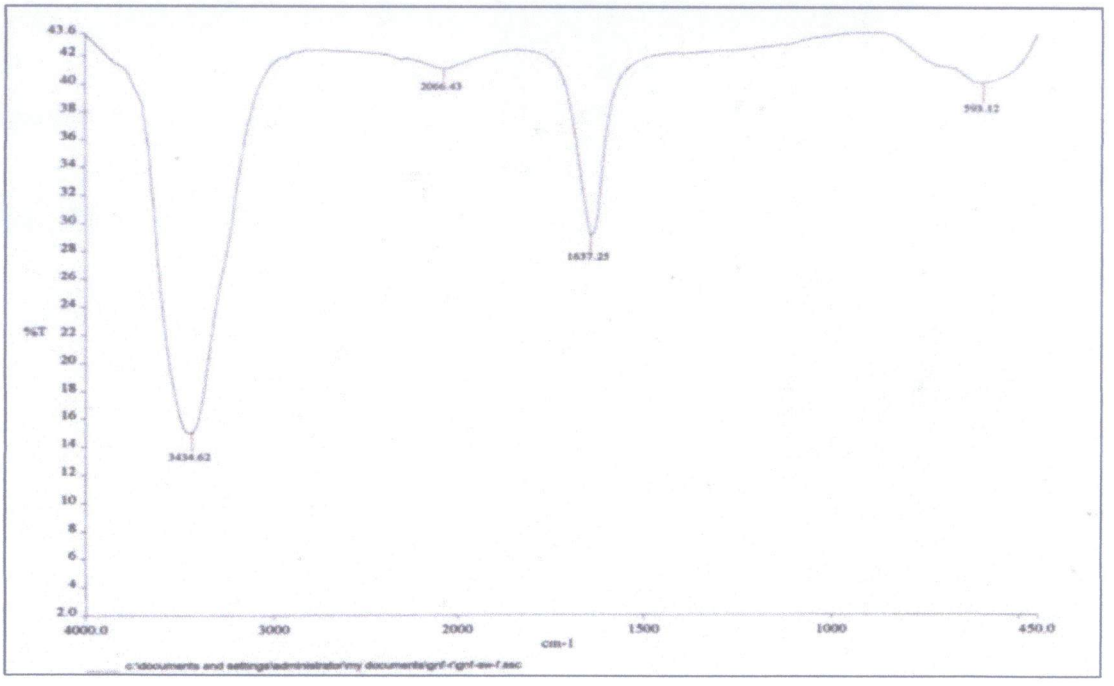



**Figure 4.2.2 : FTIR Analysis of Functionalized Graphite Nanofibers**

*Analysis*

The FTIR spectrum in Figure 4.2.2, confirm the presence of functional groups in the functionalized graphite nanofibers (GNF). For analysis of the FTIR result, the tabulated characteristic of the IR absorption from the FTIR spectra of functionalized GNF as shown in the table below. The characterization of IR absorption was obtained from various sources of IR absorption table as included in appendices section.

**Table 4.2.1: IR Absorption of Functionalized GNFs**

| Frequency, $cm^{-1}$ | Bond | Functional group |
|---|---|---|
| 593.12 | C-Br | Alkyl halides |
| 1637.25 | C=O | Carboxylic acids |
| 2066.43 | C≡C | Alkynes |
| 3434.62 | O-H | Alcohols, Phenols |

The analysis gotten was made by using FTIR analysis done by Prodana et al (2012) as guidance. The presence of the functional group like carboxylic acids in the GNF shows the functionalization with chemical treatment method was a success. The functionalized GNF exhibit a peak at 3434.62 $cm^{-1}$ is assigned to the O-H band from carboxyl groups (O=C-OH and C-OH). The peak 2066.43 $cm^{-1}$ corresponded to the C≡C stretch. Meanwhile, the peak at 1637.25 $cm^{-1}$ which can be assigned to characteristics of carboxylic groups (C=O) stretches as observed in the FTIR spectra indicating that carboxylic groups were formed due to the oxidation of some carbon atoms on the surfaces of the GNF by nitric acid. It is believed that the existing on the surface of functionalized GNF can easily interact with the functional groups on the polymer (polycarbonate) molecular chains, to form hydrogen bonds at the interface of GNF and the polymer matrix. The last peak of 593.12 $cm^{-1}$ comes from the potassium bromide used for the FTIR spectroscopy.

## 4.3 FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM)

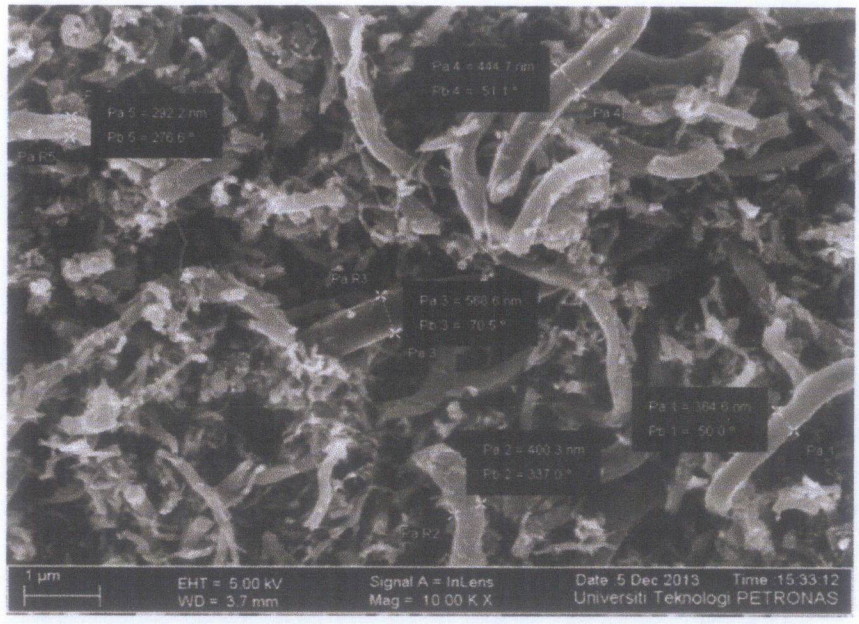



**Figure 4.3.1 : FESEM image of raw GNF at smaller magnification**

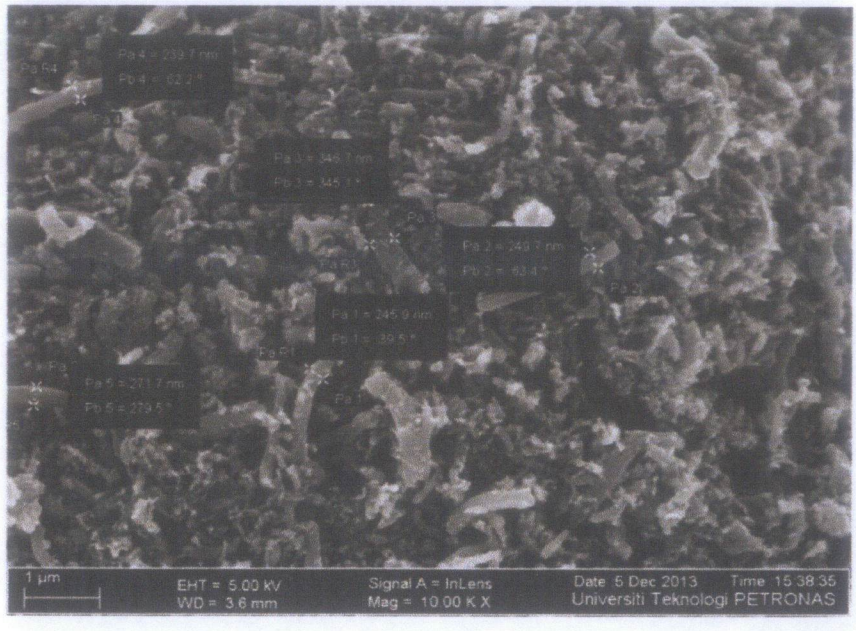



**Figure 4.3.2 : FESEM image of Functionalized GNF at smaller magnification**

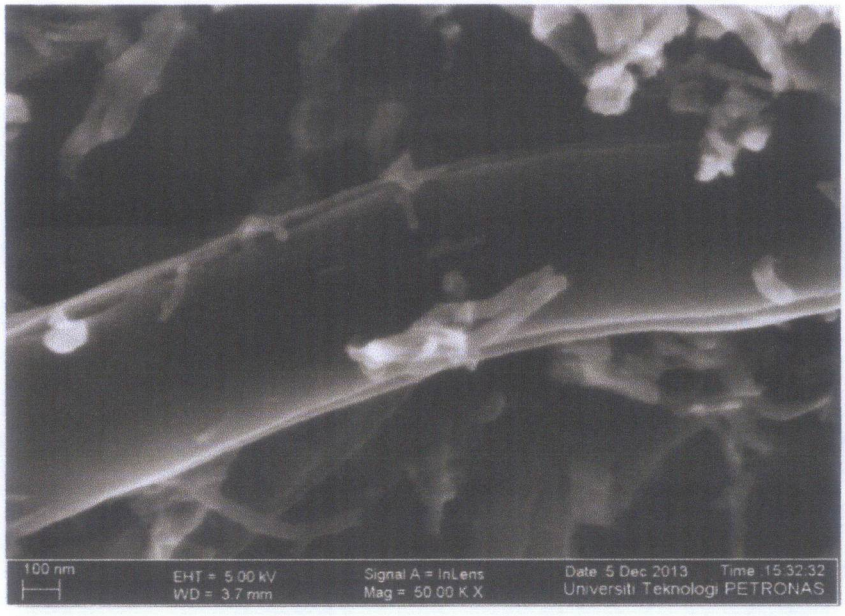



**Figure 4.3.3 : FESEM image of raw GNF at higher magnification**

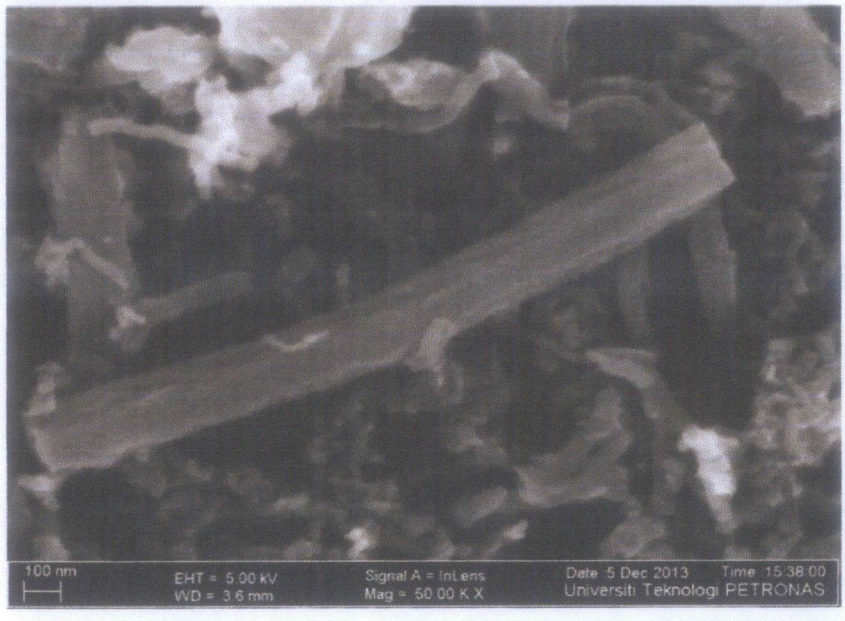



**Figure 4.3.4 : FESEM image of Functionalized GNF at higher magnification**

*Analysis*

Field Emission Scanning Electron Microscopy (FESEM) was conducted to study the size and morphology of the graphite nanofibers (GNF) before mixing the fibers with polycarbonate. This is due to the functionalization will have an effect on the surface of the fibers and their size from attaching the functional group to the surface and also the acid treatment method used to functionalize the sample. Figure 4.3.1 and Figure 4.3.2 shows the difference of raw and functionalized GNFs' sizes. The raw GNF is found to have a bigger average size at 414.1nm as compared to the functionalized GNF at 270.4nm; where the five measurements done on the raw sample to see the average size are 364.6nm, 400.3nm, 568.6nm, 444.7nm, and 292.2nm while the five measurements on the functionalized samples are 245.9nm, 249.7nm, 345.7nm, 239.7nm, and 271.7nm. Even without the values, the pictures lucidly displays that the raw GNF carry the fibrous shape or string-like shape while those of the functionalized sample looks like broken strings and small indeed. In Figure 4.3.3 and Figure 4.3.4 shows a higher magnification of the samples image and focus on a fiber. Figure 4.3.3 exhibits a fiber of raw GNF where it has a smooth surface and still have the amorphous layer around it. As for the functionalized GNF, in Figure 4.3.4, the fibers were a part of broken fiber and the surface covered with cracks. This is because, in theory, functionalization will cause the size to decrease and mass loss, besides damaging the surface of the GNF by causing cracks where the functional groups are attached proves the nanofibers were oxidized.

## 4.4 PC-GNF MICROSCOPIC IMAGING

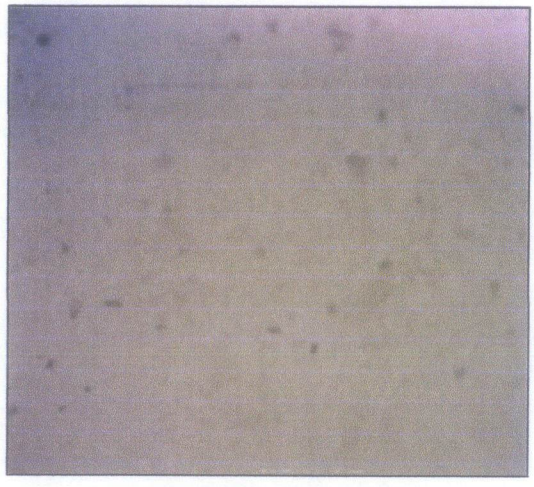


**Figure 4.4.1: Microscopic Image, PC-GNF 0.1wt%**

**Figure 4.4.2: Microscopic Image, PC-GNF 0.5wt%**

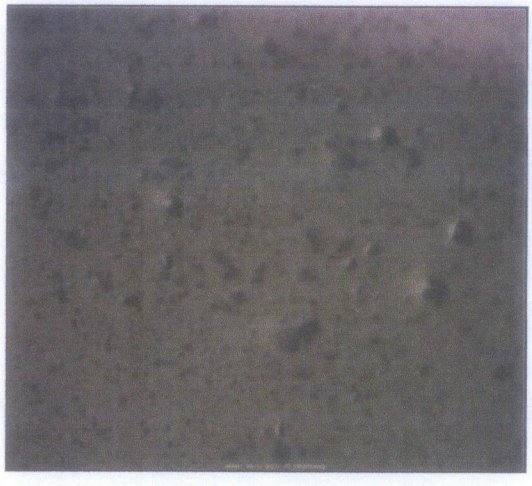


**Figure 4.4.3 : Microscopic Image, PC-GNF 1wt%**

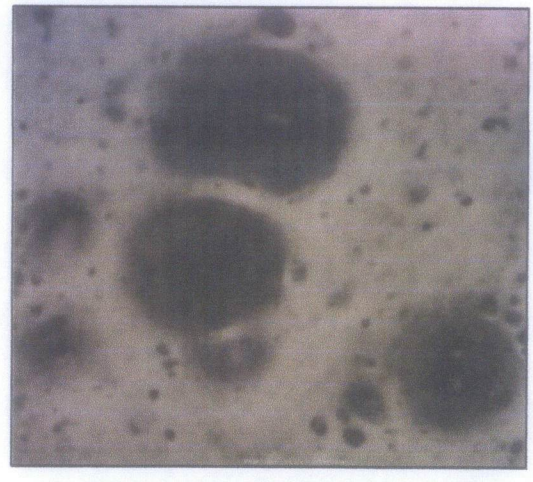
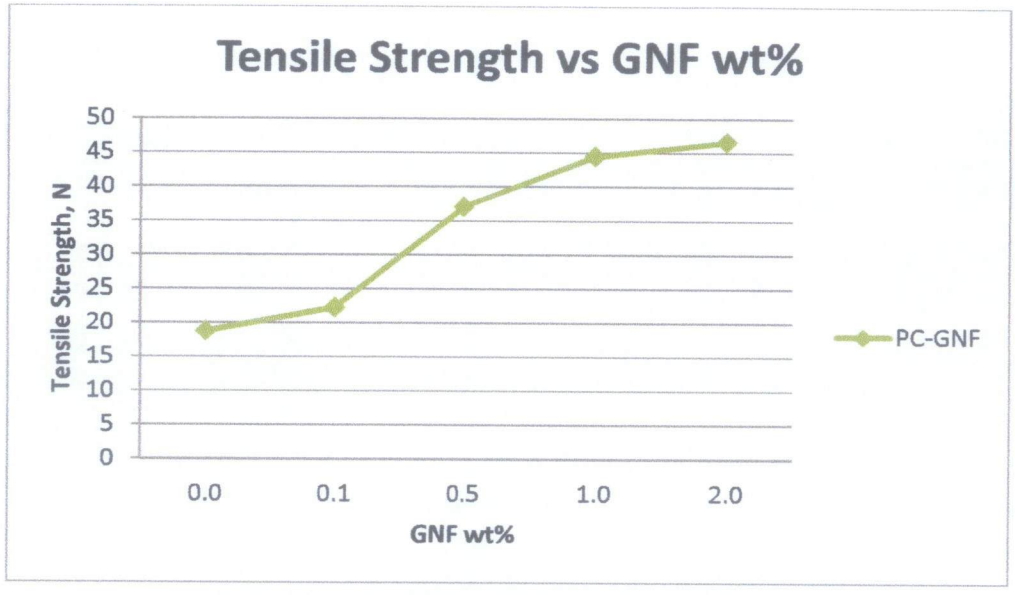


**Figure 4.4.4: Microscopic Image, PC-GNF 2wt%**

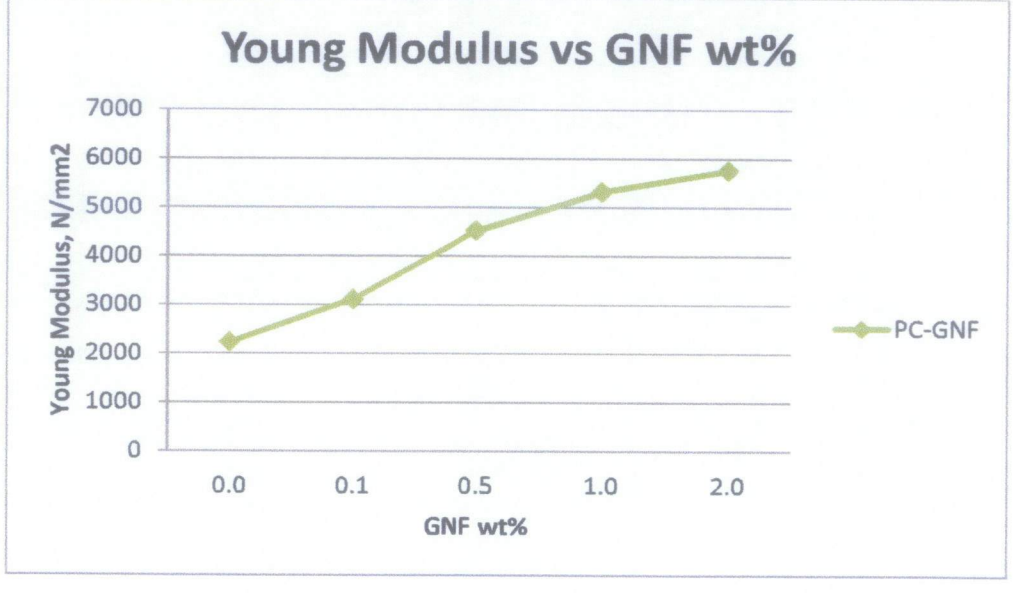
*Analysis*

To study the dispersion and the homogeneous of the PC-GNF matrix, microscopic imaging was used with 100X magnification for clearer and more detailed picture. In Figure 4.4.1, it shows the microscopic imaging of the PC-GNF with 0.1wt% of GNF. The picture displays a good dispersion; where the tiny black spots which are GNF are at distant and isolated but throughout still. Figure 4.4.2, gives the result of the microscopic image for the sample PC-GNF with 0.5wt% of GNF and it shows great dispersion and homogeneous between the GNF and polycarbonate. This homogeneous mixture gives sign of the efficient mixing and strong interaction between GNF and polycarbonate. With an increase of GNF weight percent, the distance between the fibers decreases as also have been shown by Figure 4.4.3, the image of PC-GNF with 1wt% of GNF where it can be observed evidently the nanofibers are closer to each other within the polymer and it have a good dispersion but the fibers starts to agglomerate and form bundles of fibers at a spot that produces the bigger black spots in the picture. In Figure 4.4.4, displays the image of PC-GNF with 2wt% of GNF. It shows of higher agglomeration within the polymer that could be due to the induced van der Waal forces during sonication between GNF and polymer does not exceed the existing inter fiber forces for such amount to prevent the fiber to aggregate (Kumar S. et al., 2010).

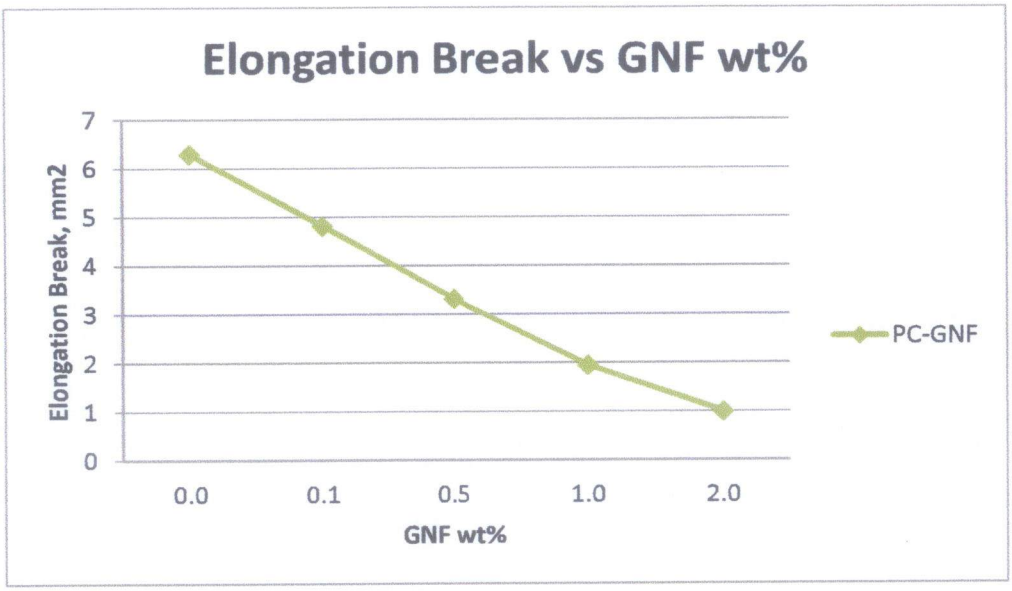
## 4.5 MECHANICAL PROPERTIES OF PC-GNF




**Graph 4.5.1 : Tensile Strength of PC-GNF vs GNFwt%**




**Graph 4.5.2 : Young Modulus of PC-GNF vs GNFwt%**




**Graph 4.5.3 : Elongation Break of PC-GNF vs GNFwt%**

**Table 4.5.1 : Mechanical Properties of PC-GNF**

| Sample | | Tensile strength | Young Modulus | Elongation Break |
|---|---|---|---|---|
| | wt% GNF | (N) | (N/mm2) | (mm) |
| PC | 0.0 | 18.8 | 2236.629 | 6.296 |
| PC-GNF | 0.1 | 22.3 | 3112.579 | 4.819 |
| PC-GNF | 0.5 | 37.1 | 4526.012 | 3.319 |
| PC-GNF | 1.0 | 44.5 | 5319.612 | 1.951 |
| PC-GNF | 2.0 | 46.6 | 5762.855 | 0.997 |

*Analysis*

To study the mechanical properties of the polymer nano-composite, the samples are put through Universal Testing Instrument to obtain their tensile strength, young modulus and elongation break. The test is performed on dumb-bell shaped samples at room temperature with gauge length 25mm, width 6mm, thickness 1.13-1.16mm and crosshead speed of 3mm/min.

The mechanical properties; tensile strength, young modulus and elongation break of pure polycarbonate (PC) and the nano-composites samples with different weight percent of graphite nanofibers (GNF) are summarized in Table 4.5.1. Figure 4.5.1 shows the relationship between tensile strength and weight percent of GNF while Figure 4.5.2 shows the correlation between young modulus and weight percent of GNF. The incorporation of GNF increases the tensile strength and young modulus with significant decrease in elongation as shown in Figure 4.5.3. The tensile strength of pure PC was increased by ≈18%, ≈97%, ≈136% and ≈143%, respectively, on incorporating 0.1wt%, 0.5wt%, 1wt%, and 2wt% of GNF into the PC matrix. The substantial increase of tensile strength with the loading of 0.5wt% suggesting a great dispersion and distribution of GNF in the polymer matrix, and where the slight increase of tensile strength at higher loadings imply that the dispersion were poor and due to the aggregation formation (Kim, K. & Jo, W., 2009) as can be seen in the FESEM. Same goes with the young modulus where the pure PC's young modulus was increased by ≈39%, ≈102%, ≈137% and ≈157%, respectively, on incorporating 0.1wt%, 0.5wt%, 1wt%, and 2wt% of GNF into the PC matrix. The dispersion and agglomeration phenomena also explain the trend of the elongation break. By increasing the GNF weight percent in PC-GNF nano-composites, it gradually decreases the elongation break indicating the reduction effect of flexibility and increase in brittleness in nano-composites.

## 4.6 THERMO GAVIMETRIC ANALYSIS (TGA) FOF PC-GNF

**Table 4.6.1 : Decomposition Onset Temperature and Maximum Weight loss Temperature for Pure PC and PC-GNF Samples**

| Sample | $T_o$ (°C) | $T_{max}$ (°C) |
|---|---|---|
| **Pure PC** | 460 | 511 |
| **PC-GNF 0.1wt%** | 474 | 531 |
| **PC-GNF 0.5wt%** | 490 | 533 |
| **PC-GNF 1wt%** | 476 | 522 |
| **PC-GNF 2wt%** | 486 | 531 |

*Analysis*

To study the thermal properties of the samples, thermal stability of pure polycarbonate (PC) and PC-GNF nano-composites against thermal decomposition was investigated using thermo gravimetric analyzer in nitrogen gas at temperature of 30-800°C, around 8-10mg of the plastic sample cut to tiny pieces with heating rate of 20°C/min.

The dynamic TGA scans of pure PC and the nano-composites samples with different weight percent of graphite nanofibers (GNF), prepared through solution blending or casting are summarized in Table 4.6.1. The onset degradation temperature, $T_o$ corresponding to 5wt% weight loss of sample tested and $T_{max}$ corresponding to the temperature at the maximum weight loss rate. As can be seen in the table, both $T_o$ and $T_{max}$ increased with the addition of GNF in the PC-GNF nano-composites. The onset degradation temperature of pure PC is 460°C and on incorporating 0.1wt%, and 0.5wt% of GNF, the $T_o$ of PC reached to 474°C and 490°C. At 1wt% the thermal stability reduces from the lower loading due to the aggregation formed where the $T_o$ is 476°C and 486°C at 2wt%. Similar trend was observed in the case of $T_{max}$, where the pure PC with

$T_{max}$ of 508°C was appeared to increase to 531°C and 533°C for 0.1wt% and 0.5wt% of GNF loaded PC-GNF nano-composites, and reduces to 522°C for 1wt% and 531°C for 2wt%. This type of increase in thermal stability with the addition of GNF to polycarbonate polymer can be explained in the term of GNF excellent thermal properties together with PC thermoplastic flame retardant properties. Besides, the GNF presented in the polymer nano-composites restricted the intimate contact of the heat with the polymer, and reduced the diffusion of heat into the bulk of the nano-composites. The increase in weight percent of GNF in the PC-GNF nano-composites consequently creates greater shielding effect, causing the increase of the thermal stability. The results found at 1wt% and 2wt% with decreasing thermal stability potential of the nano-composites due to the aggregation of GNF formed within the samples. In addition, the metal elimination method performed beforehand helps in increasing the thermal stability by removing traces of metal catalyst in the raw GNF due to nickel catalyst used as catalyst were reported to accelerate the degradation of polymer and organic compounds because it have the potential to participate in radical formation reactions (Li Z. et al., 2011).

# CHAPTER 5
# RECOMMENDATION

**Morphology :**

For this project, there were no test done on the surface morphology of PC-GNF nano-composites samples and the detailed distribution imaging of the samples. This is due to time constraint, as sending samples to for Transmission Electron Microscopy (TEM) analysis will take a lot of time and expensive in cost as FESEM cannot be used as it only scan through the surface of the samples and not within. It is suggested that for such project, for it to be more convincing and effective, the samples morphology and nano-composite structure needed to be study, because the dispersion and distribution of nanofibers in the polymer matrix will highly affected their properties.

**Wider GNF loading variables :**

In this project, due to limited time and resources, only four different GNF loading variables were afford to be experimented but with more time and money allocation for the research, more loading variables should be investigated. This will enable to see the trends of properties focusing on lower loading and higher loading. Not to mention, it will create a more resounding deduction of results.

**Other property testings :**

More tests can be done to check on the thermal and mechanical properties such as, Differential Scanning Calorimetry (DCS) to get the melting temperature, and glass temperature, Dynamic Mechanical Analyzer (DMA) to determine the storage modulus, and stress-strain test. Besides, electrical property tests should be done as GNF have great electrical properties that it would offer to the PC-GNF nano-composites.

# CHAPTER 6
# CONCLUSION

The nano-enhanced transparent thermoplastic polycarbonate with functionalized graphite nanofibers have been successfully been prepared by solution blending technique. The FTIR results revealed the functionalized GNF have functional groups attached which supported with the morphological studies from the FESEM images that shows cracks on the surface where the carboxyl group located. This was then proved by the samples' ability to sustain being dispersed for a day. The microscopic imaging displays a good dispersion of GNF within the polymer nano-composites and at 1wt% and 2wt% of GNF, aggregations of fibers were found; which results in 0.5wt% being the optimum weight percent that produced the best increase in mechanical and thermal properties. The mechanical properties exhibit increases in tensile strength and young modulus with the increase loading of GNF but reduce the elongation ability. The thermal stability of polycarbonate was also found to improve with the addition of GNF and the aggregation formation reduces the potential of thermal stability. The new improved properties, without drastically change the color in the PC-GNF nano-composites and maintaining transparency may yield up to a new era of application in polycarbonate within a more varied industries.

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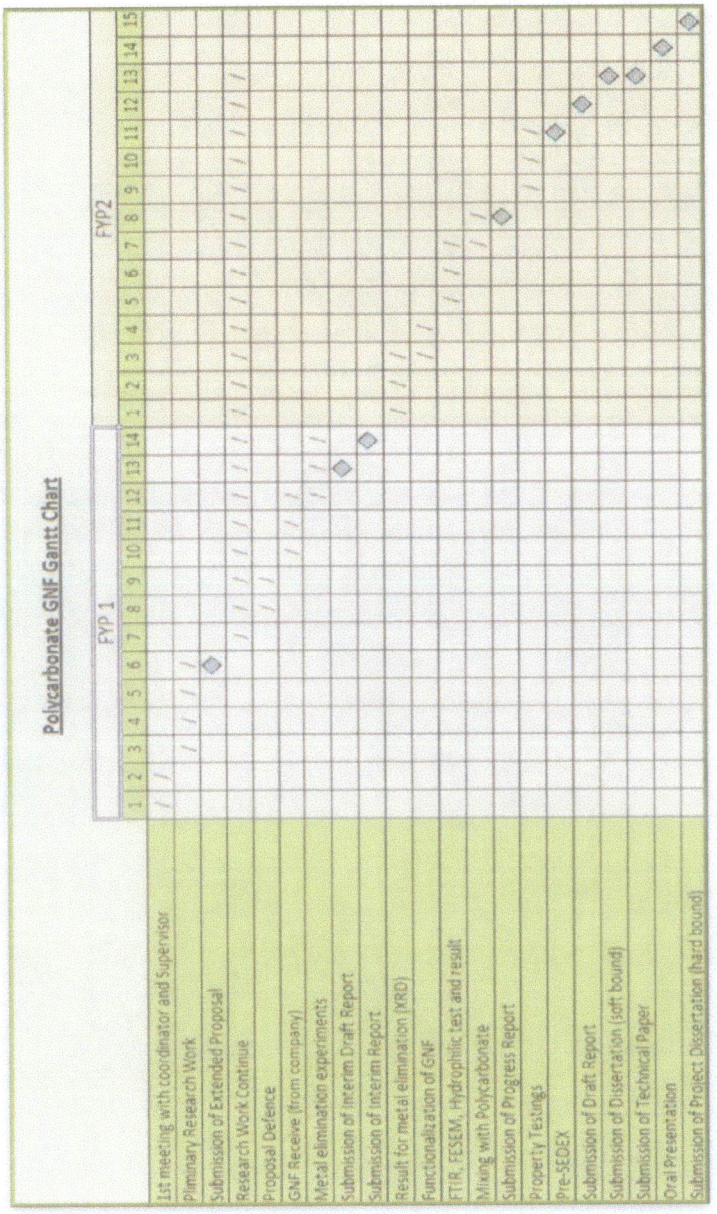
# APPENDICES

## Appendix I

Table 6.1: Polycarbonate GNF Blending Gantt Chart



## Appendix II

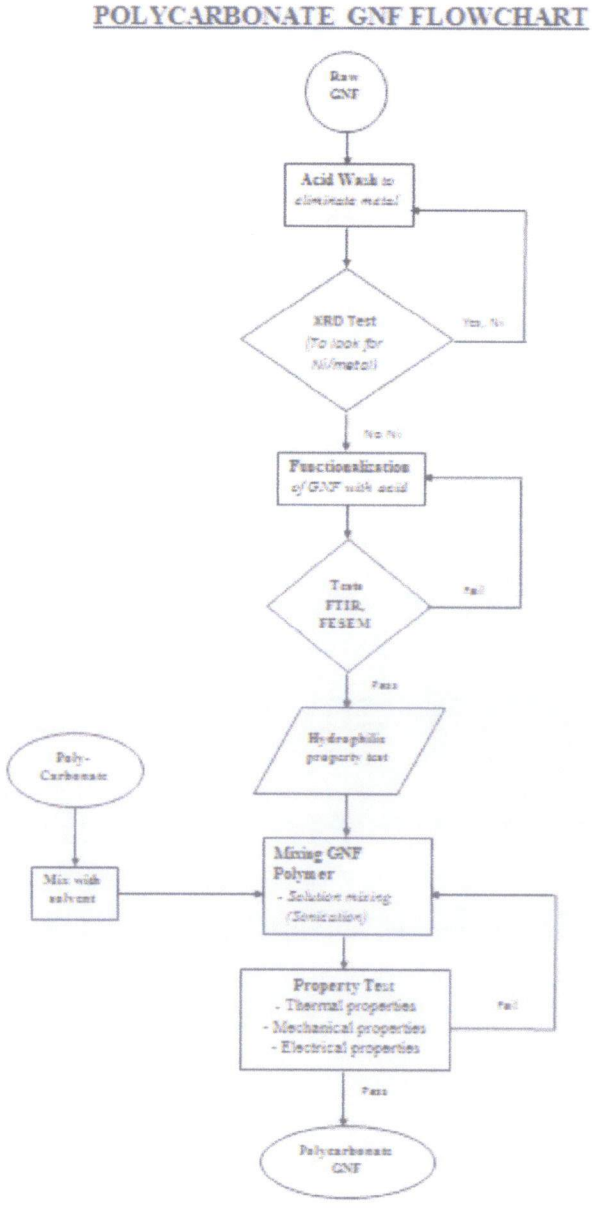



Figure 6.1: Polycarbonate GNF Flowchart

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# Appendix III

## Table 6.2 :Table of Characteristic of IR Absorptions I

**Table of Characteristic IR Absorptions**

| *frequency, cm$^{-1}$* | *bond* | *functional group* |
|---|---|---|
| 3640–3610 (s, sh) | O–H stretch, free hydroxyl | alcohols, phenols |
| 3500–3200 (s,b) | O–H stretch, H–bonded | alcohols, phenols |
| 3400–3250 (m) | N–H stretch | 1°, 2° amines, amides |
| 3300–2500 (m) | O–H stretch | carboxylic acids |
| 3330–3270 (n, s) | –C≡C–H: C–H stretch | alkynes (terminal) |
| 3100–3000 (s) | C–H stretch | aromatics |
| 3100–3000 (m) | =C–H stretch | alkenes |
| 3000–2850 (m) | C–H stretch | alkanes |
| 2830–2695 (m) | H–C=O: C–H stretch | aldehydes |
| 2260–2210 (v) | C≡N stretch | nitriles |
| 2260–2100 (w) | –C≡C– stretch | alkynes |
| 1760–1665 (s) | C=O stretch | carbonyls (general) |
| 1760–1690 (s) | C=O stretch | carboxylic acids |
| 1750–1735 (s) | C=O stretch | esters, saturated aliphatic |
| 1740–1720 (s) | C=O stretch | aldehydes, saturated aliphatic |
| 1730–1715 (s) | C=O stretch | α, β–unsaturated esters |
| 1715 (s) | C=O stretch | ketones, saturated aliphatic |
| 1710–1665 (s) | C=O stretch | α, β–unsaturated aldehydes, ketones |
| 1680–1640 (m) | –C=C– stretch | alkenes |
| 1650–1580 (m) | N–H bend | 1° amines |
| 1600–1585 (m) | C–C stretch (in–ring) | aromatics |
| 1550–1475 (s) | N–O asymmetric stretch | nitro compounds |
| 1500–1400 (m) | C–C stretch (in–ring) | aromatics |
| 1470–1450 (m) | C–H bend | alkanes |
| 1370–1350 (m) | C–H rock | alkanes |
| 1360–1290 (m) | N–O symmetric stretch | nitro compounds |
| 1335–1250 (s) | C–N stretch | aromatic amines |
| 1320–1000 (s) | C–O stretch | alcohols, carboxylic acids, esters, ethers |
| 1300–1150 (m) | C–H wag (–$CH_2X$) | alkyl halides |
| 1250–1020 (m) | C–N stretch | aliphatic amines |
| 1000–650 (s) | =C–H bend | alkenes |
| 950–910 (m) | O–H bend | carboxylic acids |
| 910–665 (s, b) | N–H wag | 1°, 2° amines |
| 900–675 (s) | C–H "oop" | aromatics |
| 850–550 (m) | C–Cl stretch | alkyl halides |
| 725–720 (m) | C–H rock | alkanes |
| 700–610 (b, s) | –C≡C–H: C–H bend | alkynes |
| 690–515 (m) | C–Br stretch | alkyl halides |

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

**Table 6.3 :Table of Characteristic of IR Absorptions II**

| *Functional Group* | *Characteristic Absorption(s)* ($cm^{-1}$) | *Notes* |
|---|---|---|
| Alkyl C-H Stretch | 2950 - 2850 (m or s) | Alkane C-H bonds are fairly ubiquitous and therefore usually less useful in determining structure. |
| Alkenyl C-H Stretch<br>Alkenyl C=C Stretch | 3100 - 3010 (m)<br>1680 - 1620 (v) | Absorption peaks above 3000 $cm^{-1}$ are frequently diagnostic of unsaturation |
| Alkynyl C-H Stretch<br>Alkynyl C≡C Stretch | ~3300 (s)<br>2260 - 2100 (v) | |
| Aromatic C-H Stretch<br>Aromatic C-H Bending<br>Aromatic C=C Bending | ~3030 (v)<br>860 - 680 (s)<br>1700 - 1500 (m,m) | |
| Alcohol/Phenol O-H Stretch | 3550 - 3200 (broad, s) | See "Free vs. Hyrdogen-Bonded Hydroxyl Groups" in the Introduction to IR Spectra for more information |
| Carboxylic Acid O-H Stretch | 3000 - 2500 (broad, v) | |
| Amine N-H Stretch | 3500 - 3300 (m) | Primary amines produce two N-H stretch absorptions, secondary amides only one, and tetriary none. |
| Nitrile C≡N Stretch | 2260 - 2220 (m) | |
| Aldehyde C=O Stretch<br>Ketone C=O Stretch<br>Ester C=O Stretch<br>Carboxylic Acid C=O Stretch<br>Amide C=O Stretch | 1740 - 1690 (s)<br>1750 - 1680 (s)<br>1750 - 1735 (s)<br>1780 - 1710 (s)<br>1690 - 1630 (s) | The carbonyl stretching absorption is one of the strongest IR absorptions, and is very useful in structure determination as one can determine both the number of carbonyl groups (assuming peaks do not overlap) but also an estimation of which types. |
| Amide N-H Stretch | 3700 - 3500 (m) | As with amines, an amide produces zero to two N-H absorptions depending on its type. |

## Appendix IV

1. Metal Elimination (Acid Wash)

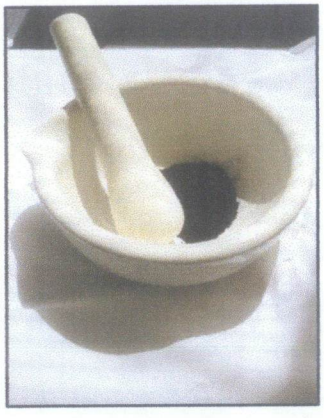

**Figure 6.2: Grinding Raw GNF**

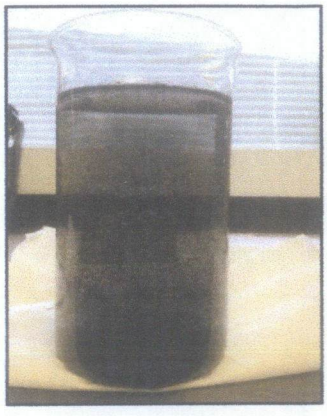

**Figure 6.3: Neutralizing after Acid Wash**

2. Functionalization

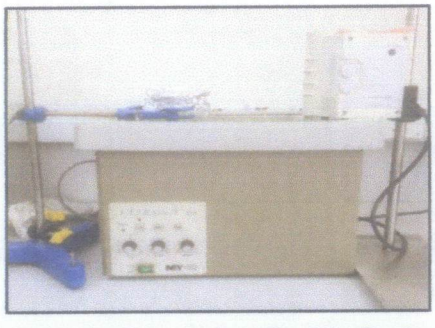

**Figure 6.4: Front-view Double Sonication Method**

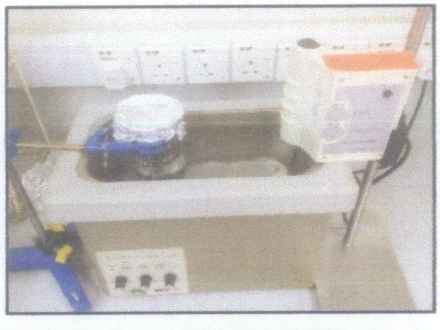

**Figure 6.5: Top-view Double Sonication Method**

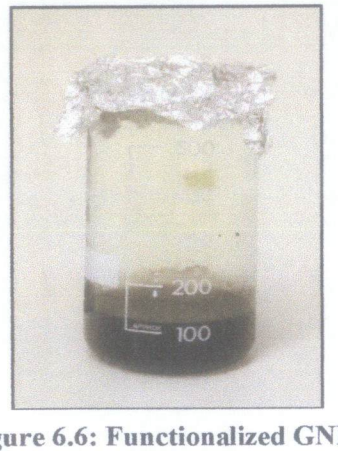


**Figure 6.6: Functionalized GNF After Sonication**

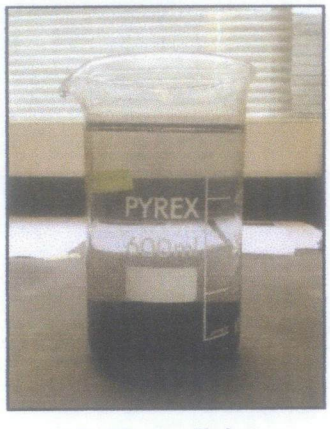


**Figure 6.7: Neutralizing Functionalized GNF**

3. Dispersion Test

**Figure 6.8: Preparation of Dispersion Test**

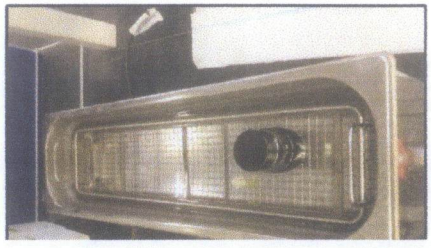

**Figure 6.9: Sonication to Disperse GNF in Methylene Chloride**

4. Polycarbonate solution Blending

**Figure 6.10: Drying Polycarbonate**

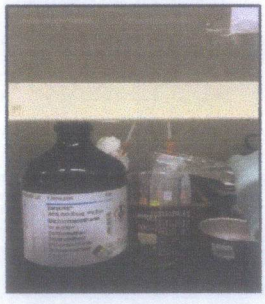

**Figure 6.11: Measuring Methylene Chloride**

**Figure 6.12: Dissolving Polycarbonate in Methylene Chloride**

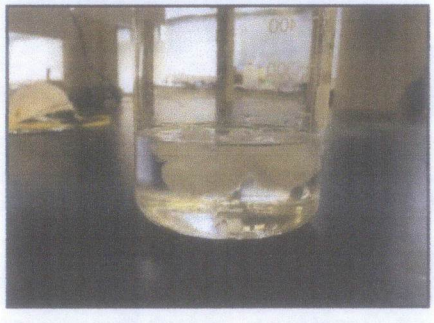

**Figure 6.13: Undissolved Polycarbonate**

**Figure 6.14: Sonication of the Undissolved Polycarbonate**

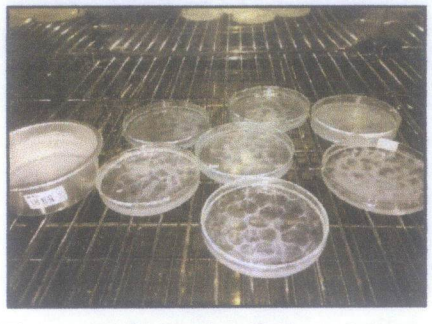

**Figure 6.15: Setting Polycarbonate in Vacuum Oven**

Pictures of Analysis/Testings

1. FTIR Preparation

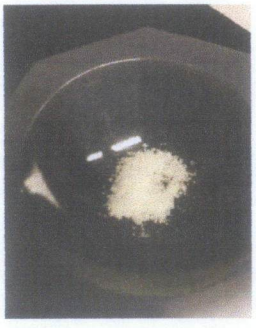

Figure 6.16: Grind and mix GNF and KBr

Figure 6.17: Compressing the mixture

Figure 6.18: FTIR equipment

2. Mechanical Testing

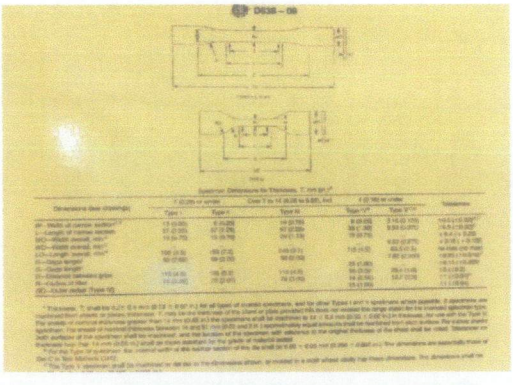

Figure 6.19: Dumb-bell shaped guidelines

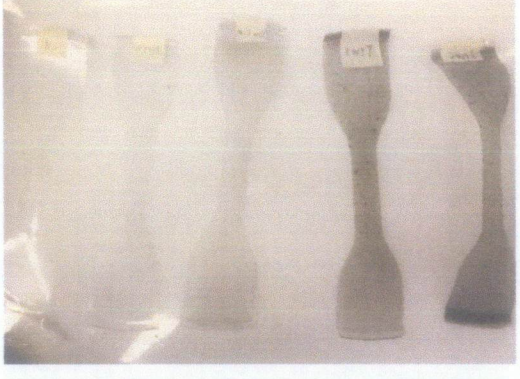

Figure 6.20: Dumb-bell shaped PC-GNF samples

Figure 6.21: Mechanical testing using Universal Testing Instrument

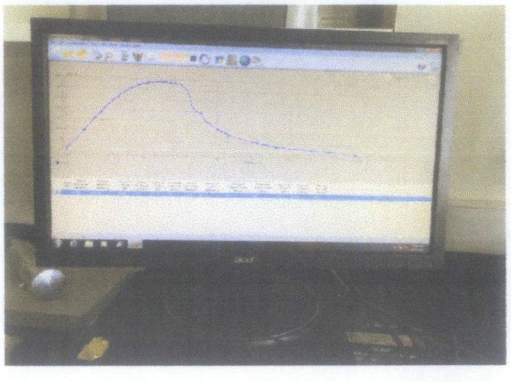

Figure 6.22: Mechanical properties results